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**MODELING OF EQUILIBRIUM  
GAS ADSORPTION FOR MULTICOMPONENT  
VAPOR MIXTURES**

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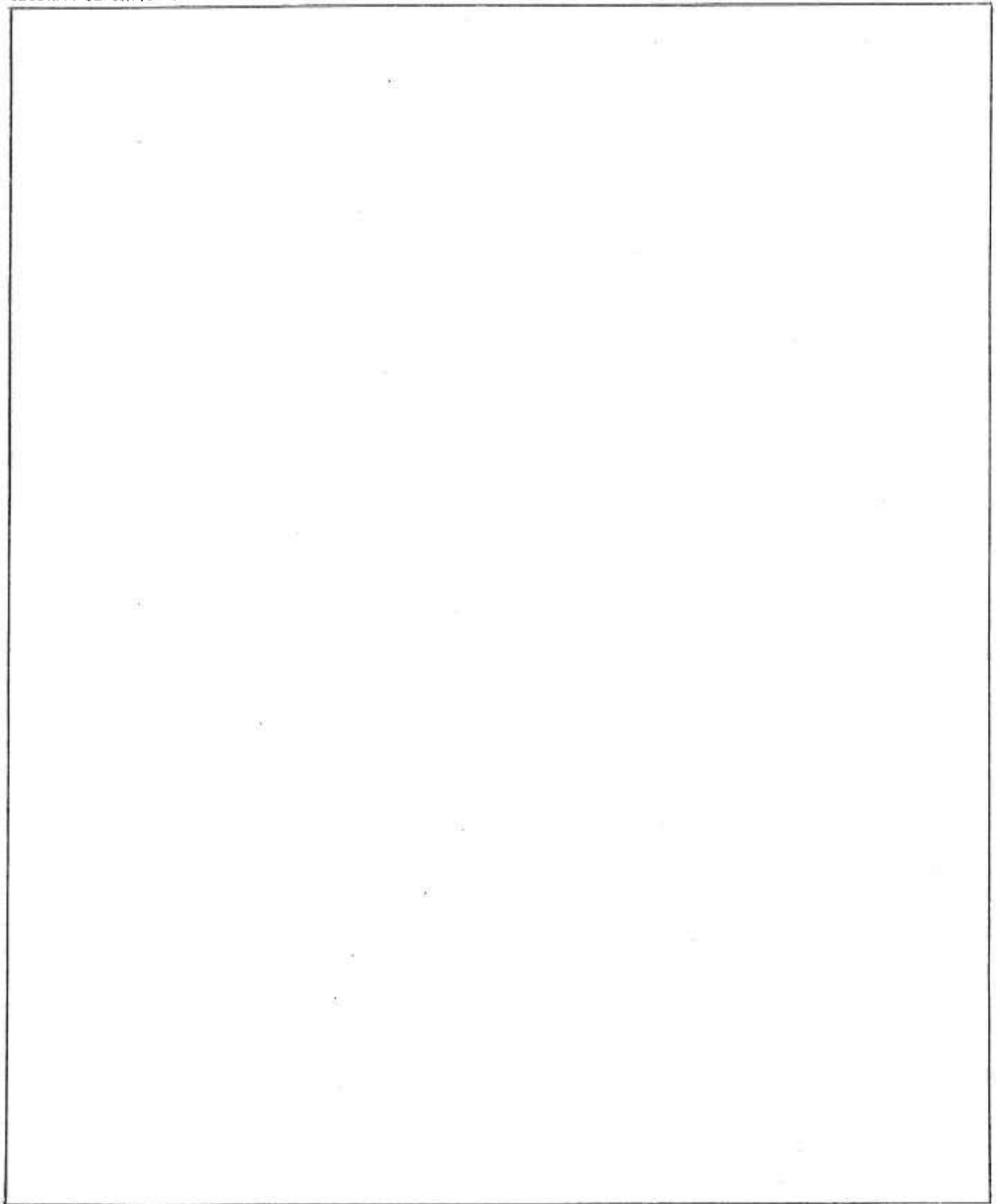
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## MODELING OF EQUILIBRIUM GAS ADSORPTION FOR MULTICOMPONENT VAPOR MIXTURES

### 1. INTRODUCTION

Single vapor equilibrium adsorption isotherms are often used to assess the relative efficiencies with which adsorbents, such as activated carbon, remove specific vapors from air in air purification schemes. Single vapor adsorption isotherms can often be predicted at equilibrium, subject to some limitations, from the physical properties of the adsorbate vapors by techniques based upon the Dubinin-Polanyi concept of affinity coefficient.<sup>1-4</sup> Past studies have provided vast amounts of adsorption isotherm data for single vapor adsorption on various adsorbents. However, the practical conditions under which adsorbents are employed are usually quite different from the ideal laboratory conditions under which the single vapor isotherms are determined. For example, several adsorbate species are usually present. The vapor species to be adsorbed may not be exposed to the adsorbent under conditions where equilibrium can be readily attained. The study of multicomponent kinetic and equilibrium adsorption on an adsorbent is very important; however, kinetic and equilibrium adsorption studies are still at a very preliminary stage while mixed vapor adsorption studies are more complex and time consuming. This problem can be alleviated to some extent if mixed adsorption isotherms can be predicted from single vapor adsorption data.

Although there has been considerable study involving the thermodynamic properties of adsorbates on adsorbents, relatively few studies have considered adsorption kinetics. Studies to date<sup>5-7</sup> have dealt with the kinetics of single vapor adsorption behavior. Many of these studies have made use of Wheeler's approach to the kinetics of gas adsorption by beds of

adsorbent granules. However, the method has yet to be applied to multicomponent systems.

The development of experimental methods for determining binary adsorption isotherms and the kinetics of binary mixture adsorption was completed in the first year of the project. In the past year, the adsorption of  $\text{CHCl}_3/\text{CCl}_4$ , n-Hexane/Benzene, and  $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$  binary systems on BPL-activated carbon was investigated. BPL is a designation assigned by Calgon Corporation. Results and conclusions from these studies will be presented in addition to recommendations for work to be carried out in future phases of the project.

## 2. BACKGROUND

### 2.1 Equilibrium Adsorption of Mixtures.

Currently, there are three potentially useful models available which have had limited success in predicting the adsorption characteristics of mixtures:

- a. Dubinin-Polanyi Pore Filling Theory<sup>1</sup>
- b. John's mixture isotherm model<sup>8</sup>
- c. Myer's ideal adsorption solution theory<sup>9</sup>

#### 2.1.1 Dubinin-Polanyi Pore Filling Theory.

The Dubinin-Polanyi theory has not been used much to predict multicomponent adsorption. The results that are available indicate, however, that the theory has some potential for application to multicomponent adsorption. Bering and co-workers<sup>10,11</sup> extended the Dubinin-Polanyi equation to the adsorption of mixtures by using the following equation:

$$\Sigma a_i = \frac{W_o}{\Sigma N_i \bar{v}_i} \exp \left[ -BT^2 \left( \frac{\Sigma N_i \log(p_{si}/p_i)}{(\Sigma N_i \bar{\beta}_i)} \right)^2 \right] \quad (1)$$

where  $\bar{v}_i$  = the partial molar volume of mixture component i

$\bar{\beta}_i$  = the partial molar affinity coefficient of mixture component i

$p_{si}$  = the saturated vapor pressure of mixture component i

$p_i$  = the equilibrium pressure of mixture component i

$a_i$  = the number of g mole of component i adsorbed per gm of adsorbent

$N_i$  = the mole fraction of component i in the adsorbed phase

$W_o$  and B = constants characterizing the adsorbent

In practice, the quantity  $\sum N_i \bar{v}_i$  can be found from the phase diagram of the volume solution assuming a liquid-like adsorbate, while  $\sum N_i \bar{\beta}_i$  can be found simply according to an additive scheme.<sup>12</sup>

In the theory of micropore filling in the case of an individual component, a normal liquid at the given temperature, existing in equilibrium with its saturated vapor at the pressure,  $P_o$ , is selected as the standard state. In the case of multicomponent adsorption, it is unclear, a priori, whether the state of a solution whose composition is equal to the composition of the adsorbed phase or the state of a solution existing in equilibrium with vapor whose composition is equal to the composition of the equilibrium vapor above the adsorbed phase should be selected as the standard state. However, studies<sup>11</sup> have shown that equation (1) is fulfilled well in both methods of selecting the standard state. Selecting such standard states, we can rewrite equation (1) for a binary mixture of vapors in the following form:

$$W = a_{12} v_{12} = W_o \exp \left[ \frac{-BT^2}{2\beta_{12}} \left( \log \left( \frac{1}{h} \right) \right)^2 \right] \quad (2)$$

where,

$$h = \frac{\sum p_i}{\sum p_{si}} = \frac{p_1}{p_{s1}} = \frac{p_2}{p_{s2}}$$

Equation 2 was found to be applicable to several systems.<sup>13,14</sup>

### 2.1.2 John's Mixture Isotherm Model.

This model, which was developed by John and others,<sup>8</sup> assumes that the single vapor isotherms for species  $i$  can be represented by the following equation:

$$\log \log P_i^0 = C_i + D_i \log W_i^0 \quad (3)$$

where  $C_i$  = a constant

$D_i$  = a constant

$W_i^0$  = amount of adsorbate in  $\text{cm}^3/\text{g}$  at pressure,  $p_i$

$P_i^0 = (p_i/p_{si}) 10^N$

and superscript 'o' denotes pure component.  $N$  = an integer between 2 and 6.

A similar equation describes the binary vapor (components 1 and 2) adsorption isotherm:

$$\log \log P_{12} = C_{12} + D_{12} \log W_{12} \quad (4)$$

where  $C_{12} = Y_1 C_1 + Y_2 C_2$

$D_{12} = Y_1 D_1 + Y_2 D_2$

$W_{12}$  = the amount of mixed adsorbate

$P_{12} = (p_1 + p_2)/(p_{s1} + p_{s2}) 10^N$

and  $Y_1$  and  $Y_2$  are the mole fractions of components 1 and 2 in the gas phase.

The constants  $C_1$ ,  $C_2$ ,  $D_1$ , and  $D_2$  can be obtained from the single vapor isotherms and then used to calculate  $W_{12}$ , in Equation 4, using known or assumed  $P_{12}$  values.

From the model, the micropore volume,  $W_0$ , can be computed for a single vapor component  $i$  as follows:

$$\log W_0 = (\log \log 10^N - C_i)/D_i \quad (5)$$

Similarly the micropore volume in the binary mixture case is given by:

$$\log W_o = (\log \log 10^N - C_{12})/D_{12} \quad (6)$$

John and others<sup>8</sup> have shown that this method can be applied to binary and ternary systems to compute their total adsorption.

### 2.1.3 Ideal Adsorbed Solution Theory .

The ideal adsorbed solution theory has been used to predict mixed gas adsorption with some success at low coverages/low relative pressure.<sup>9,15</sup> The method assumes that the adsorbed phase forms an ideal solution and involves determining the 'spreading pressure' for the single vapor isotherms. The calculation is made as follows:

- a. Obtain the single vapor isotherms for pure components in terms of the amount absorbed, (cc/g) versus equilibrium pressure (torr).
- b. The spreading pressure for these adsorbates is calculated as follows:

$$\frac{\pi A}{RT} = \int_0^P \frac{n}{p_i^o} dp_i^o \quad (7)$$

where  $\pi$  = spreading pressure

$A$  = specific area of adsorbent

$n$  = total number of moles in adsorbed phase/gm of adsorbent

$p_i^o$  = equilibrium vapor pressure of pure component

- c. Calculate the vapor pressure of pure components at constant spreading pressure.

- d. Describe the amount adsorbed ( $n_i^o$ ) at these vapor pressures (calculated in step c) from step a.

- e. Calculate the adsorption equilibria for both components at a desired total pressure,  $P$ , using the following two equations:

$$Py_1 = p_1^o N_1 \quad (8)$$

$$Py_2 = p_2^o N_2 \quad (9)$$

Adding these two equations, the expression for an ideal liquid solution is obtained.

$$N_1 = \frac{P - p_2^o}{p_1^o - p_2^o} \quad (10)$$

The vapor phase composition is given by:

$$Y_1 = \frac{p_1^o N_1}{P} \quad (11)$$

$N_1$  is the mole fraction of component 1 in the adsorbed phase and  $Y_1$  is the mole fraction of component 1 in the gas phase.

f. The total amount adsorbed is obtained by:

$$\frac{1}{n} = \sum \frac{N_i}{n_i^o} \quad (12)$$

g. Finally, the amount of each component adsorbed from the gas mixture is given by:  $n_i = nN_i$ .

The complete isobaric composition diagram for any mixture is obtained by repeating the above calculation for different values of the spreading pressure.

## 2.2 Kinetics of Adsorption.

Studies on the kinetics of adsorption on activated carbon have been previously reported<sup>5-7</sup> for the case of single vapor adsorption but have yet to be extended to multicomponent mixtures. However, many of the mathematical equations and kinetic processes which describe these phenomena for single vapors should also be applicable to multicomponent mixtures. Of particular interest is the approach taken by Wheeler<sup>16,17</sup> which has been used successfully for single vapor adsorption kinetics.<sup>5-7</sup> Wheeler's



equation, which is based on the principle of mass conservation, can be written as follows:

$$t_b = (W_e/C_o Q)[W_b - \rho_B Q \ln(C_o/C_x)/k_V] \quad (13)$$

where  $C_o$  = the inlet gas concentration in  $\text{g/cm}^3$

$k_V$  = the first order rate constant in  $\text{min}^{-1}$

$\rho_B$  = the bulk density of packing in  $\text{g/cm}^3$

$W_e$  = the kinetic saturation capacity in  $\text{g/g}$

$W_b$  = the bed weight in gm

$Q$  = the volume flow rate in  $\text{cm}^3/\text{min}$

$t_b$  = the breakthrough time in min

and  $C_x$  is the exit gas concentration.

From a plot of  $t_b$  versus  $W_b$ , the saturation capacity ( $W_e$ ) and the first order rate constant ( $k_V$ ) can be obtained. By setting  $t_b$  of Equation (13) equal to zero and solving for  $W_b$  one obtains

$$W_b = \frac{\rho_B Q}{k_V} \ln \left( \frac{C_o}{C_x} \right) = W_c \quad (14)$$

where  $W_c$  is identified as the critical bed weight, or that weight of carbon just sufficient to reduce  $C_o$  to  $C_x$  under the test conditions.

### 3. WORK OBJECTIVES

The ultimate objectives of the study are to develop methods for predicting the adsorptive behavior of mixed gas systems on activated carbon adsorbents from a knowledge of the adsorptive properties of the pure components and to determine applicability of the Wheeler equation to multi-component kinetic adsorption.

The work has been divided into the following four phases: (1) determination of equilibrium adsorption isotherms on BPL-activated carbon for various binary vapor mixtures at  $25^\circ\text{C}$ , (2) prediction of binary vapor

adsorption isotherms on BPL-activated carbon for comparison with experimentally determined isotherms, (3) determination of breakthrough parameters through adsorbent beds for single vapors and binary vapor mixtures, and (4) testing the applicability of Wheeler's equation to binary systems.

#### 4. PROCEDURES AND RESULTS

##### 4.1 Binary Equilibrium Adsorption .

The apparatus and experimental procedures used for measuring the single and binary vapor adsorption isotherms have been described in a previous report by Reucroft and others.<sup>18</sup>

The activated carbon was a Pittsburgh-activated carbon, type BPL, 12-30 mesh, having an internal surface area of about 1000 m<sup>2</sup>/g and approximately 80% of the internal surface area associated with pores less than 20Å in diameter.

Three experimental procedures were previously evaluated to determine a precise method for measuring the adsorption characteristic of the binary mixtures. In methods A and B, individual mixtures containing various relative pressures (0.10, 0.15, 0.20, 0.25, and 0.30) of each component were made prior to exposure to the carbon.

In method A, the same sample was used for each exposure, with outgassing and drying being employed between each exposure. In method B, a fresh carbon sample was dried and outgassed prior to each exposure. In method C, a mixture containing 0.3 P/P<sub>0</sub> of each component was made and the mixture was introduced as if it were a single vapor. It was concluded that Method A was inaccurate since a residual amount of vapor could not be outgassed under heating (300°C) and vacuum (10<sup>-5</sup> torr). In Method C, it was assumed that the gases mix ideally and behave like a single vapor since the relative volume of the two gases adsorbed is very small compared to the total volume of gases. This assumption is valid since the mixed adsorption

isotherms obtained by both methods B and C are in good agreement as shown in Figure 1. Since method B is very time consuming compared to method C, we have elected to use method C for our adsorption studies.

#### 4.2 Results and Discussion

The  $\text{CHCl}_3$ ,  $\text{CCl}_4$  single vapor, and  $\text{CHCl}_3/\text{CCl}_4$  mixed vapor adsorption isotherms are shown in Figure 2 in terms of amount adsorbed ( $\text{gg}^{-1}$ ) versus relative vapor pressure. These mixed ( $\text{CHCl}_3/\text{CCl}_4$ ) isotherm data were obtained by Method C. As shown in Figure 3, the amount adsorbed ( $W_{12}$ ,  $\text{gg}^{-1}$ ) is a linear function of chloroform mole fraction in the gas phase. These mixed isotherms were also predicted using the pore filling isotherm model and John's isotherm model. The adsorption isotherm data obtained from experiments and the predicted isotherm data using the pore filling model and John's model are listed in Tables 1 and 2 and shown graphically in Figures 4 and 5. Although both models underpredict the total amount adsorbed at higher pressures, the experimental results and the model predictions are in good agreement at lower pressures.

It is important to be able to predict the amount of each binary component adsorbed when the amount of mixture adsorbed ( $W_{12}$ ) is known. The semi-empirical function of Lewis<sup>19</sup> can be used, in principle, to predict the amount of each binary component adsorbed:

$$\frac{W_1}{W_1^0} + \frac{W_2}{W_2^0} = 1 \quad (15)$$

where  $W_1 + W_2 = W_{12}$  and  $W_1$ ,  $W_2$  and  $W_{12}$  are the amounts adsorbed of component 1, component 2 and the mixture at pressures

$$p_{12} = p_1^0 = p_2^0. \quad (\text{Note } p_{12} = p_1 + p_2) \quad (16)$$

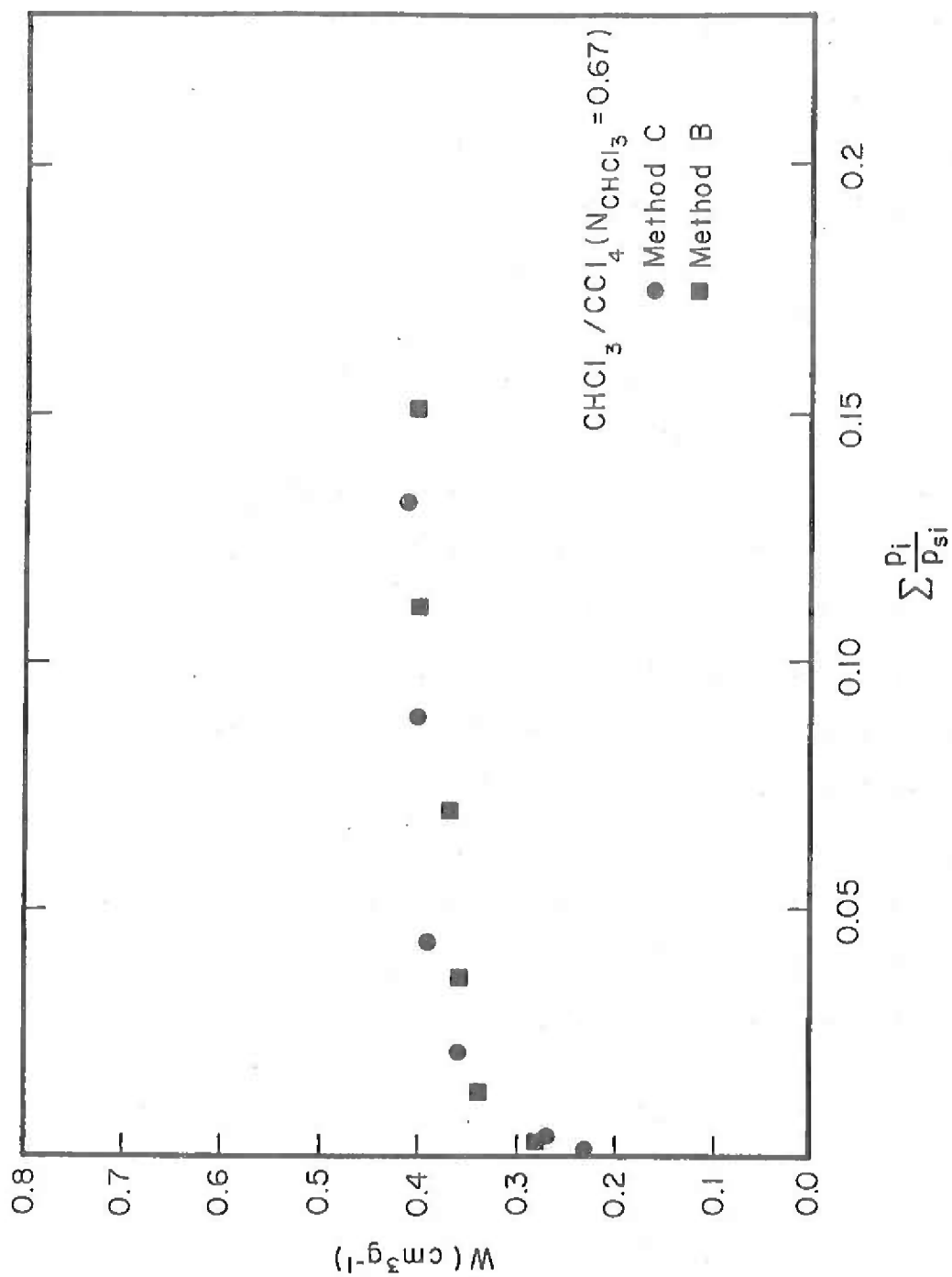


Figure 1. Adsorption of CHCl<sub>3</sub>/CCl<sub>4</sub> Binary Vapor Mixture on BPL-Activated Carbon Using Methods B and C

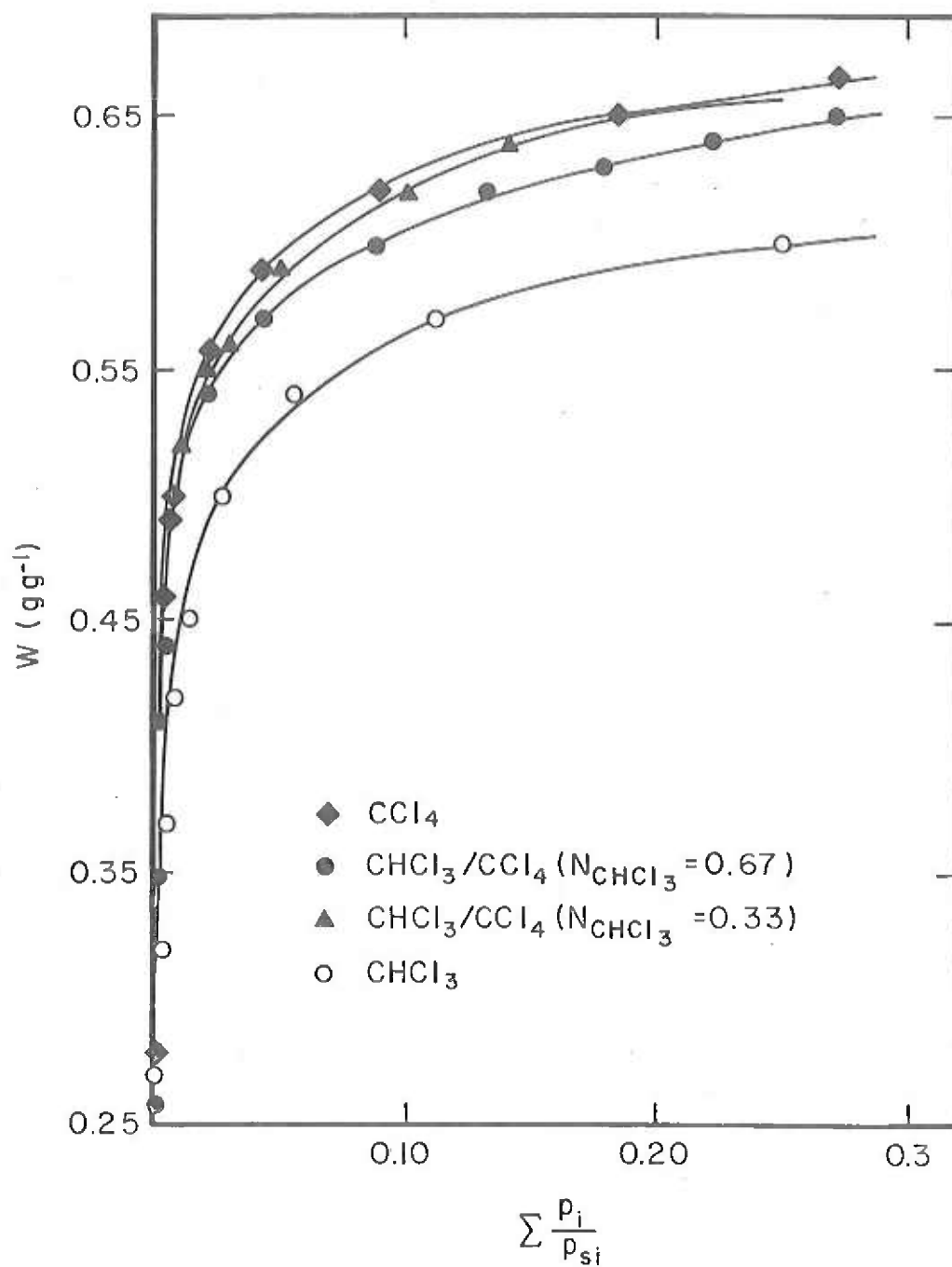


Figure 2. Adsorption Equilibria of Binary Gas Mixture ( $\text{CHCl}_3/\text{CCl}_4$ ) on BPL-Activated Carbon at 25°C

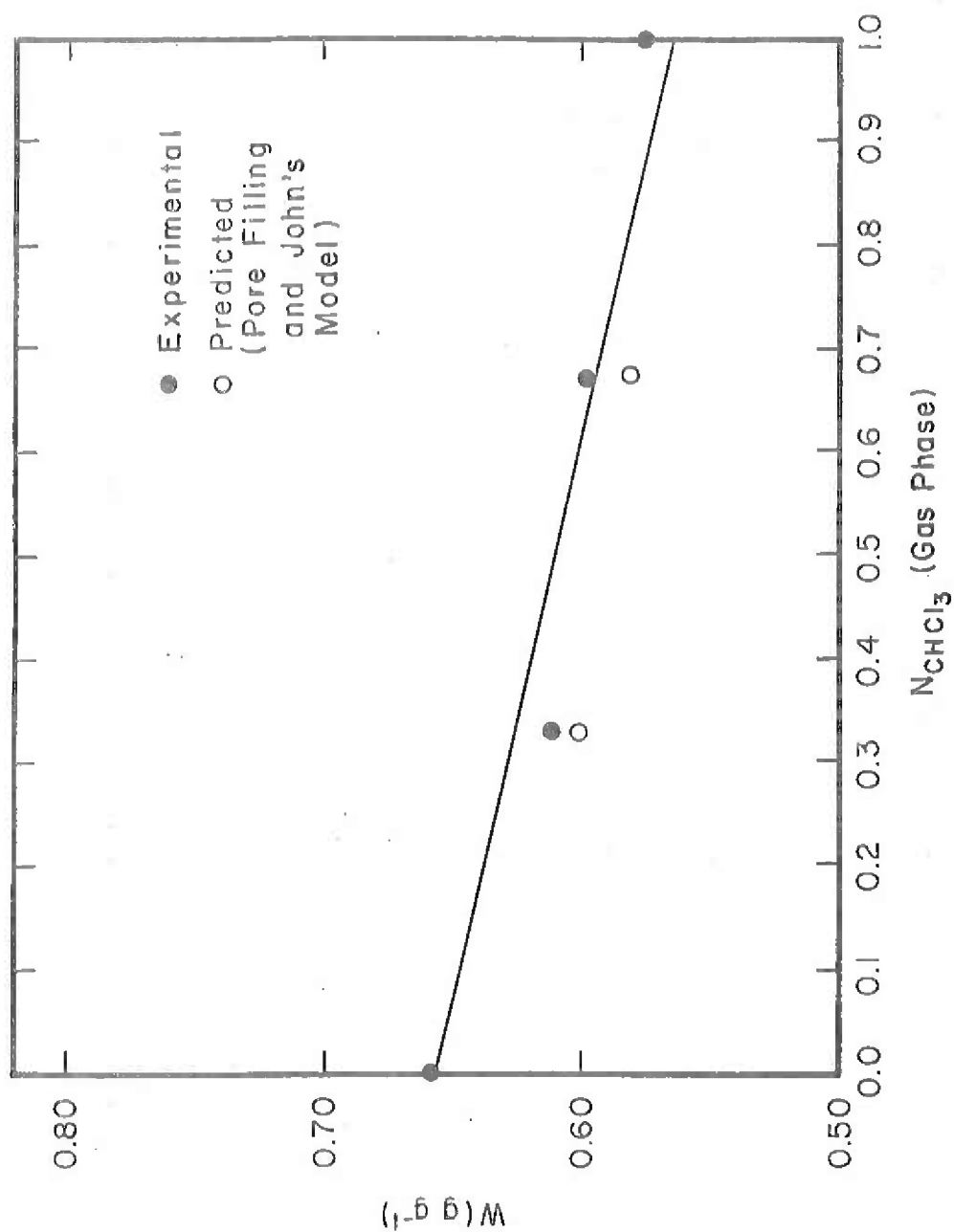


Figure 3. The Total Amount of  $\text{CHCl}_3/\text{CCl}_4$  Adsorbed on BPL-Activated Carbon at  $25^\circ\text{C}$  and a Total Pressure of 25 Torr as a Function of  $\text{CHCl}_3$  Mole fraction

Table 1. Experimental and Predicted  $W$  ( $\text{cm}^3 \text{g}^{-1}$ ) Values ( $\text{CHCl}_3/\text{CCl}_4$  System)  
 Using John's Model and Pore Filling Model (Mole Fraction of  
 $\text{CHCl}_3 = 0.67$ , BPL-Activated Carbon at  $25^\circ\text{C}$ , Density =  $1.52 \text{ g cm}^{-3}$ )

$\sum \frac{P_i}{P_{si}}$	Amount Adsorbed ( $\text{W cm}^3 \text{g}^{-1}$ )		
	Experimental	Predicted Values	
		John's Model	Pore Filling Model
0.0133	0.3390	0.3117	0.3440
0.0260	0.3600	0.3436	0.3607
0.034	0.3680	0.3530	0.3668
0.069	0.3920	0.3757	0.3810
0.111	0.4050	0.3896	0.3889
0.149	0.4140	0.3977	0.3931
0.223	0.4230	0.4084	0.3979
0.280	0.4300	0.4100	0.4001

Table 2. Experimental and Predicted  $W$  ( $\text{cm}^3 \text{g}^{-1}$ ) Values ( $\text{CHCl}_3/\text{CCl}_4$  System)  
 Using John's Model and Pore Filling Model (Mole Fraction of  
 $\text{CHCl}_3 = 0.33$ , BPL-Activated Carbon at  $25^\circ\text{C}$ , Density =  $1.56 \text{ g cm}^{-3}$ )

$\sum \frac{P_1}{P_{si}}$	Amount Adsorbed ( $W \text{ cm}^3 \text{g}^{-1}$ )		
	Experimental	Predicted Values	
		John's Model	Pore Filling Model
0.002	0.290	0.2174	0.2963
0.005	0.315	0.2826	0.3229
0.010	0.330	0.3159	0.3414
0.020	0.350	0.3428	0.3583
0.050	0.378	0.3725	0.3772
0.080	0.380	0.3859	0.3853
0.100	0.398	0.3919	0.3887
0.150	0.412	0.4023	0.3942
0.200	0.422	0.4094	0.3974
0.250	0.430*	0.4147	0.3996

\*Extrapolated Value.



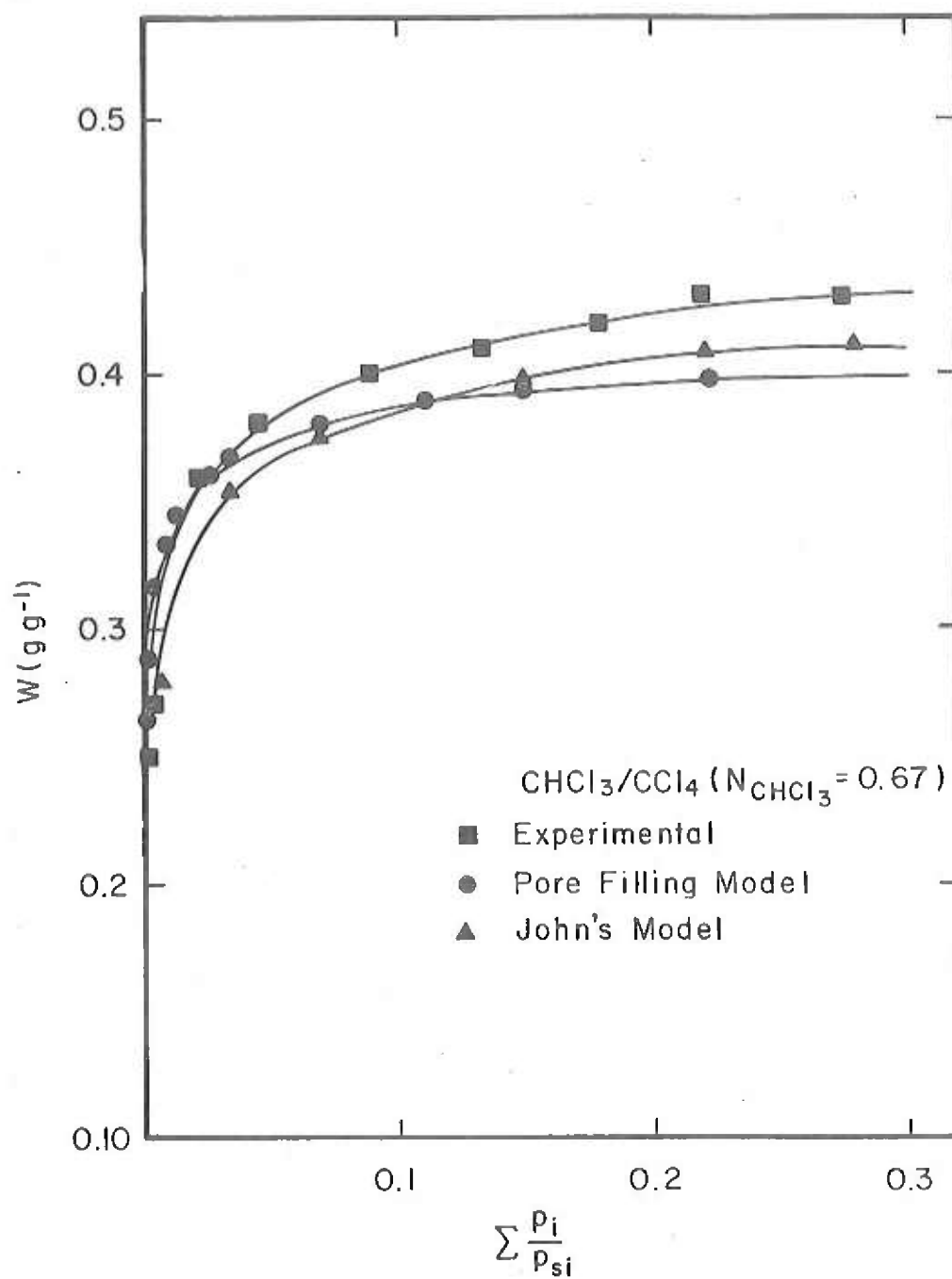


Figure 4. Experimental and Predicted Values of Total Adsorption of  $\text{CHCl}_3/\text{CCl}_4$  Binary Vapor Using Pore Filling and John's Model (Mole Fraction of  $\text{CHCl}_3$  in Gas Phase = 0.67, Temperature = 25°C, and BPL-Activated Carbon)

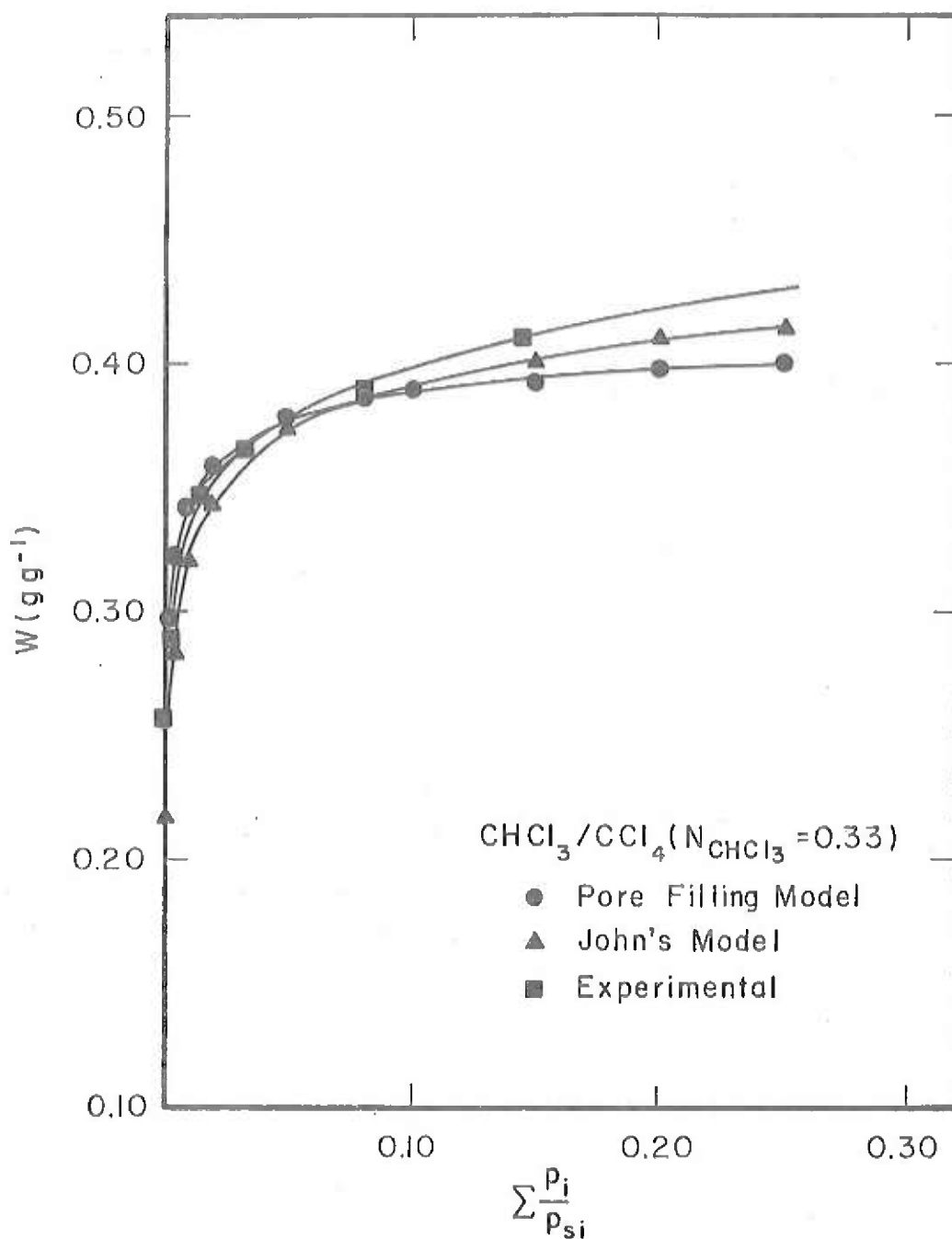


Figure 5. Experimental and Predicted Values of Total Adsorption of CHCl<sub>3</sub>/CCl<sub>4</sub> Binary Vapor Using Pore Filling and John's Model (Mole Fraction of CHCl<sub>3</sub> in Gas Phase = 0.33, Temperature = 25°C, BPL-Activated Carbon)

The values of the mixture components ( $\text{CHCl}_3$  and  $\text{CCl}_4$ ) calculated according to the above equations are marked by solid points in Figure 6. As can be seen from Figure 6, the values of  $\text{CHCl}_3$  and  $\text{CCl}_4$  calculated in this way show a linear dependence on the mole fraction of  $\text{CHCl}_3$  in the gas phase.

#### 4.3 Kinetics of Adsorption.

The experimental procedure and a schematic of the binary vapor test apparatus used for determining the kinetics of adsorption were described in an earlier report by Reucroft and others.<sup>18</sup> The concentration of each component was determined from the traced area of the gas chromatograph peaks. The ratio of the exit concentration,  $C_x$ , to the inlet concentration,  $C_o$ , was plotted as a function of time,  $t$ . The time when the breakthrough concentration reaches  $0.01 C_o$  ( $C_x/C_o = 0.01$ ) is defined as the breakthrough,  $t_b$ . The exact breakthrough time ( $t_b$ ) was determined as a function of carbon weight and composition of gas mixture.

#### 4.4 Results and Discussion.

A typical breakthrough curve for all the single vapor runs shows a sigmoidal shape curve. However, in the case of the binary vapor mixture, a vapor which is being displaced does not follow this behavior, as evident from the  $C_x/C_o$  ratio being greater than 1.0. A linear regression analysis of the  $t_b$  versus  $W_b$  data (Tables 3-5) for several binary and single vapor systems in terms of the Wheeler equation leads to the determination of  $W_e$ ,  $W_o$ , and  $k_v$ . Tables 6-10 show these parameters for three binary systems ( $\text{CHCl}_3/\text{CCl}_4$ ,  $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ , and n-hexane/benzene). In the case of the  $\text{CHCl}_3/\text{CCl}_4$  and  $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$  binary systems, the experimental kinetic saturation capacity,  $W_e$ , tends to show total values which exceed those obtained by the direct weight method ( $W_m$ ) and equilibrium gravimetric

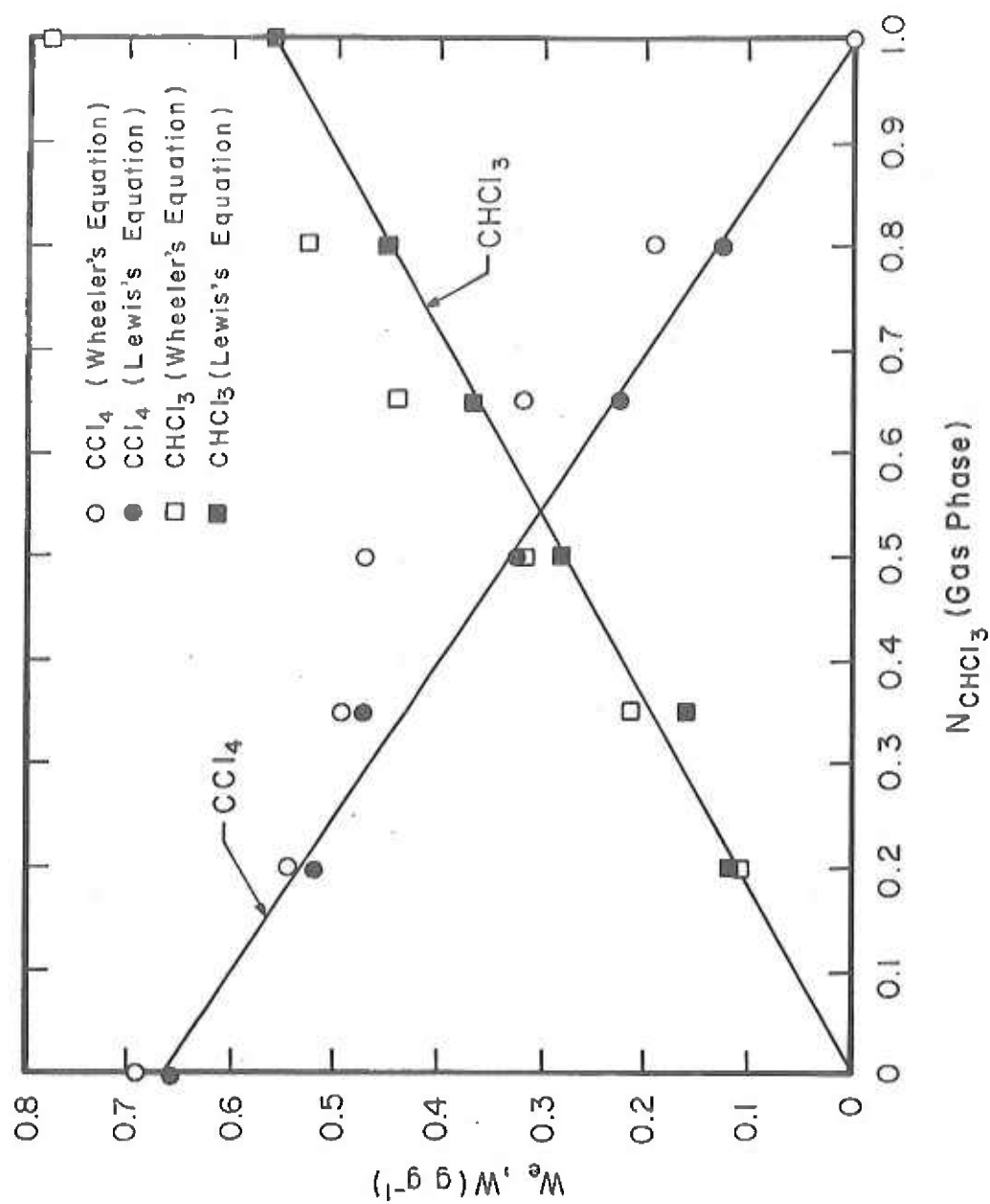


Figure 6. Effect of Composition on Adsorptive Capacity of  $\text{CHCl}_3$  and  $\text{CCl}_4$  in a Binary Mixture of  $\text{CHCl}_3/\text{CCl}_4$  (BPL-Activated Carbon)

Table 3. Breakthrough Time,  $t_b$ , as a Function of Composition and Bed Weight ( $W_b$ ) for  $\text{CHCl}_3/\text{CCl}_4$  Binary Mixtures\*

Mole fraction <sup>+</sup> $N_{\text{CHCl}_3}$	$t_b$ (min)		$W_b$ (g)	Regression Equation
	$\text{CHCl}_3$	$\text{CCl}_4$		
0.00	-	6.00	0.5823	$\text{CCl}_4: t_b = 13.98W - 2.18$ corr. = 0.9980
	-	8.30	0.7771	
	-	9.90	0.8494	
	-	12.10	1.0240	
0.20	5.10	5.20	0.6377	$\text{CCl}_4: 8.33W - 0.130$ corr. = 0.999 $\text{CHCl}_3: t_b = 8.681W - 0.576$ corr. = 0.975
	5.80	5.95	0.7318	
	6.00	6.50	0.7973	
	7.30	7.60	0.9263	
0.35	4.50	4.65	0.5925	$\text{CCl}_4: 9.9035W - 1.190$ corr. = 0.987 $\text{CHCl}_3: 9.4210W - 1.0739$ corr. = 0.998
	5.90	6.05	0.7466	
	6.85	7.20	0.8242	
	7.45	7.60	0.9163	
	8.60	9.00	1.0250	
0.50	5.20	5.70	0.6108	$\text{CCl}_4: 8.823W - 0.196$ corr. = 0.989 $\text{CHCl}_3: 8.428W - 0.086$ corr. = 0.990
	5.80	6.00	0.6810	
	7.50	7.90	0.8511	
	7.65	8.20	0.9191	
0.65	5.90	6.10	0.6380	$\text{CCl}_4: 12.6467W - 1.8812$ corr. = 0.949 $\text{CHCl}_3: 10.1801W - 0.6331$ corr. = 0.9997
	6.85	7.50	0.7374	
	8.80	10.05	0.9326	
	10.35	11.60	1.0743	
0.80	7.10	7.60	0.6856	$\text{CCl}_4: 10.898W - 0.006$ corr. = 0.972 $\text{CHCl}_3: 8.334W - 1.1930$ corr. = 0.895
	7.50	8.60	0.8111	
	9.00	10.00	0.8986	
1.00	7.90	-	0.6310	$\text{CHCl}_3: 12.05W - 0.188$ corr. = 0.9859
	8.80	-	0.7520	
	10.70	-	0.8670	
	11.70	-	0.9868	

\*BPL-Activated Carbon, Flow Rate = 400  $\text{cm}^3/\text{min}$ , 25°C, and  $P_{\text{total}} = 25$  torr.

<sup>+</sup>Vapor Phase

Table 4. Breakthrough Time,  $t_b$ , as a Function of Composition and Bed Weight ( $W_b$ ) for  $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$  Binary Mixtures\*

Mole fraction <sup>+</sup> $^N\text{CH}_2\text{Cl}_2$	$t_b$ (min)		$W_b$ (g)	Regression
	$\text{CH}_2\text{Cl}_2$	$\text{CHCl}_3$		
0.00	-	7.00	0.7000	$\text{CHCl}_3: t_b = 12.1646W_b - 1.5738$ corr. = 0.9998
	-	10.50	1.0003	
	-	12.75	1.1787	
	-	15.50	1.3994	
0.35	6.05	7.50	0.6998	$\text{CH}_2\text{Cl}_2: t_b = 12.1153W_b - 2.6001$ corr. = 0.9975
	7.45	10.20	0.8498	
	12.00	17.90	1.1990	$\text{CHCl}_3: t_b = 21.0484W_b - 7.4179$ corr. = 0.9990
0.50	6.00	8.60	0.7017	$\text{CH}_2\text{Cl}_2: t_b = 12.5388W_b - 3.0496$ corr. = 0.9960
	4.05	15.20	1.000	
	14.70	23.70	1.4007	$\text{CHCl}_3: t_b = 21.5806W_b - 6.4839$ corr. = 0.9999
0.65	6.00	10.45	0.7004	$\text{CH}_2\text{Cl}_2: t_b = 10.8161W_b - 1.6632$ corr. = 0.9984
	8.95	16.45	0.9992	
	11.90	21.00	1.2441	$\text{CHCl}_3: t_b = 19.4891W_b - 2.9901$ corr. = 0.9971
1.00	5.95	-	1.0013	$\text{CH}_2\text{Cl}_2: t_b = 7.0211W_b - 1.2902$ corr. = 0.9964
	7.55	-	1.3007	
	9.55	-	1.5505	
	12.05	-	1.8818	

\*BPL-Activated Carbon, Flow Rate =  $400 \text{ cm}^3/\text{min}$ ,  $25^\circ\text{C}$ , and  $P_{\text{total}} = 25 \text{ torr}$ .

<sup>+</sup>Vapor Phase

Table 5. Breakthrough Time,  $t_b$ , as a Function of Composition and Bed Weight ( $W_b$ ) for n-Hexane/Benzene Binary Mixtures\*

Mole Fraction <sup>+</sup> $N_n$ -Hexane	$t_b$ (min)		$W_b$ (g)	Regression
	n-Hexane	Benzene		
0.0	-	5.15	0.8000	Benzene:
	-	6.00	0.9037	$t_b = 7.7743W_b - 1.0403$
	-	7.55	1.1006	
	-	9.85	1.4033	corr. = 0.9999
0.2	4.50	4.50	0.8004	Benzene: $t_b = 7.4478W_b - .0839$
	5.95	5.95	1.0020	corr. = .9998
	7.40	7.50	1.2032	n-Hexane: $t_b = 7.1996W_b - 1.2630$ corr. = 1.0000
0.50	3.75	4.10	0.7005	Benzene:
	4.45	4.50	0.8515	$t_b = 6.1813W_b - 0.6835$
	5.55	5.85	1.0018	corr. = 0.998
	6.65	6.90	1.2001	
	8.10	8.40	1.4097	n-Hexane: $t_b = 6.2459W_b - 0.5003$
0.80	3.70	3.20	0.7019	Benzene:
	4.45	4.15	0.8502	$t_b = 10.1161W_b - 4.1374$
	7.10	9.20	1.3109	corr. = 0.9961
				n-Hexane: $t_b = 5.6232W_b - 0.2830$ corr. = 0.9997
1.00	4.2	-	0.5997	n-Hexane:
	4.5	-	0.6875	$t_b = 8.1474W_b - 1.049$
	5.9	-	0.8498	corr. = 0.9998
	7.1	-	0.9934	
	10.35	-	1.4028	

\*BPL-Activated Carbon, Flow Rate = 400 cm<sup>3</sup>/min, 25°C, and  $P_{total}$  = 25 torr.

<sup>+</sup>Vapor Phase

Table 6. Equilibrium and Dynamic Adsorption Data for  $\text{CHCl}_3/\text{CCl}_4$  Mixture on BPL-Activated Carbon ( $P_{\text{total}} = 25$  torr, Flow Rate =  $400 \text{ cm}^3 \text{ min}^{-1}$ , and Temperature =  $25^\circ\text{C}$ )

Mole Fraction $N_{\text{CHCl}_3}$ (in Vapor Phase)	$W_e$ (g/g)		Total $W_e$ (g/g)	$W_m$ (g/g)	$W_g$ (g/g)
	$\text{CHCl}_3$	$\text{CCl}_4$			
0.00	-	0.6962	0.6962	0.5674	0.6281
0.20	0.1255	0.6605	0.7860	0.5560	0.6240
0.35	0.2148	0.4944	0.7092	0.5799	0.6200
0.50	0.3198	0.4758	0.7956	0.5454	0.6080
0.65	0.4398	0.3288	0.7686	0.5602	0.6000
0.80	0.5305	0.1916	0.7221	0.5327	0.5820
1.00	0.7815	-	0.7813	0.5047	0.5700

Table 7. Equilibrium and Dynamic Adsorption Data for n-Hexane/Benzene Mixture on BPL-Activated Carbon ( $P_{\text{total}} = 25$  torr and Flow Rate =  $400 \text{ cm}^3/\text{min}$ )

Mole Fraction $N_{\text{n-Hexane}}$ (in vapor phase)	$W_e$ (g/g)		Total $W_e$ (g/g)	$W_m$ (g/g)	$W_g$ (g/g)
	n-Hexane	Benzene			
0.0	-	0.3300	0.3300	0.350	0.37
0.2	0.0666	0.2501	0.3167	0.335	-
0.5	0.1298	0.1444	0.2742	0.311	-
0.8	0.2040	0.0894	0.2974	0.284	-
1.0	0.2260	-	0.2260	0.250	0.27



Table 8. Equilibrium and Dynamic Adsorption Data for  $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$  Binary System on BPL-Activated Carbon ( $P_{\text{Total}} = 25$  torr and Flow Rate =  $400 \text{ cm}^3/\text{min}$ )

Mole Fraction $N_{\text{CH}_2\text{Cl}_2}$ (in vapor phase)	$W_e$ (g/g)		Total $W_e$ (g/g)	$W_m$ (g/g)
	$\text{CH}_2\text{Cl}_2$	$\text{CHCl}_3$		
0.0	-	0.7813	0.7813	0.5012
0.35	0.1937	0.8786	1.0723	0.5253
0.50	0.2864	0.6929	0.9793	0.5157
0.65	0.3212	0.4380	0.7592	0.4993
1.0	0.5132	-	0.5132	0.4517

Table 9. Experimental and Predicted Saturation Capacity Using John's and Pore Filling Model ( $\text{CHCl}_3/\text{CCl}_4$  Binary System,  $P_{\text{total}} = 25$  torr, Flow Rate =  $400 \text{ cm}^3/\text{min}$ , and Temperature =  $25^\circ\text{C}$ )

Mole Fraction * $N_{\text{CHCl}_3}$	$W_e$ (g/g)	$W_g$ (g/g)		$W_m$ (g/g)	$W_g$ (g/g)
		Pore Filling Model	John's Model		
0.00	0.6962	0.6644	0.6552	0.5674	0.6580
0.20	0.7860	0.6355	0.6093	0.5560	-
0.35	0.7092	0.6284	0.5997	0.5799	0.6130
0.50	0.7361	0.6212	0.5897	0.5454	-
0.65	0.7686	0.6140	0.5794	0.5602	0.6020
0.80	0.7221	0.6068	0.5687	0.5327	-
1.00	0.7813	0.6084	0.5737	0.5047	0.5760

\* Vapor Phase

Table 10. Experimental and Predicted Saturation Capacity Values Using John's Model and Pore Filling Model (n-Hexane/Benzene Binary System,  $P_{\text{total}} = 25$  torr, Flow Rate =  $400 \text{ cm}^3/\text{min}$ , and Temperature =  $25^\circ\text{C}$ )

Mole Fraction $N_{\text{Hexane}}$	$W_e$ (g/g)	$W_g$ (g/g)		$W_m$ (g/g)
		Pore Filling Model	John's Model	
0.0	0.3300	-	-	0.350
0.2	0.3167	0.3261	0.3191	0.335
0.5	0.2742	0.3168	0.3019	0.311
0.8	0.2994	0.2918	0.3260	0.284
1.0	0.226	-	-	0.25

values ( $W_g$ ). However, in the case of the n-hexane/benzene binary system, the  $W_e$  values agree very well with  $W_m$  and  $W_g$ . Moreover, the  $W_e$  values for the n-hexane/benzene and the  $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$  systems generally increase with increasing concentration of the more volatile component.

In all three systems, it was observed that the component with higher saturated vapor pressure in a binary system is displaced regardless of the relative value of its polarity or affinity coefficient. Also, the  $W_e$  values for all single vapors obtained from Wheeler's equation at the same total pressure (25 torr) agree very well with  $W_m$  and  $W_g$  values, with the exception of  $\text{CHCl}_3$  vapor (see Table 11). It is clear that the Wheeler equation is not as effective when it is applied to vapors such as  $\text{CHCl}_3$  and binary systems with  $\text{CHCl}_3$  as a component.

The breakthrough time of  $\text{CHCl}_3$  is faster than that of  $\text{CCl}_4$  in  $\text{CHCl}_3/\text{CCl}_4$  mixtures but is slower than that of  $\text{CCl}_4$  in single vapor determinations. Similarly, the breakthrough time of n-hexane is faster than that of benzene in n-hexane/benzene mixtures, but is slower than that of benzene in single vapor determinations. In the breakthrough studies on  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  displayed the faster breakthrough time in all situations.

The mole fractions of the more volatile components in the adsorbed phase were calculated from the  $W_e$  values. These values, as a function of the mole fraction of the same component in the gas phase are shown in Figures 7-9. From this set of data, it appears that the mole fraction of  $\text{CHCl}_3$  in the adsorbed phase is similar in value to the mole fraction of  $\text{CHCl}_3$  in the gas phase.

Figure 7 also shows that the ideal adsorbed solution theory<sup>9</sup> which was used previously to predict mixed gas adsorption equilibria from single vapor sorption isotherms of the individual components, does not predict

Table 11. Kinetic versus Equilibrium Saturated Capacity for Single Vapors at 0.1 Relative Vapor Pressure and 25°C  
(BPL-Activated Carbon, Flow Rate = 400 cm<sup>3</sup>/min)

Vapor	Saturation Capacity (g/g)		$W_{\max}^*$ (g/g)	$W_m$ (g/g)
	$W_e$ (g/g)	$W_g$ (g/g)		
CCl <sub>4</sub>	0.696	0.6281	0.6678	0.5674
CHCl <sub>3</sub>	0.7813	0.5700	0.6586	0.5047
CH <sub>2</sub> Cl <sub>2</sub>	0.5132	-	-	0.4517
N-Hexane	0.2260	0.2680	0.2805	0.2500
Benzene	0.307	0.3426	0.3778	0.3300

\*Maximum capacity of carbon (from equilibrium gravimetric studies)

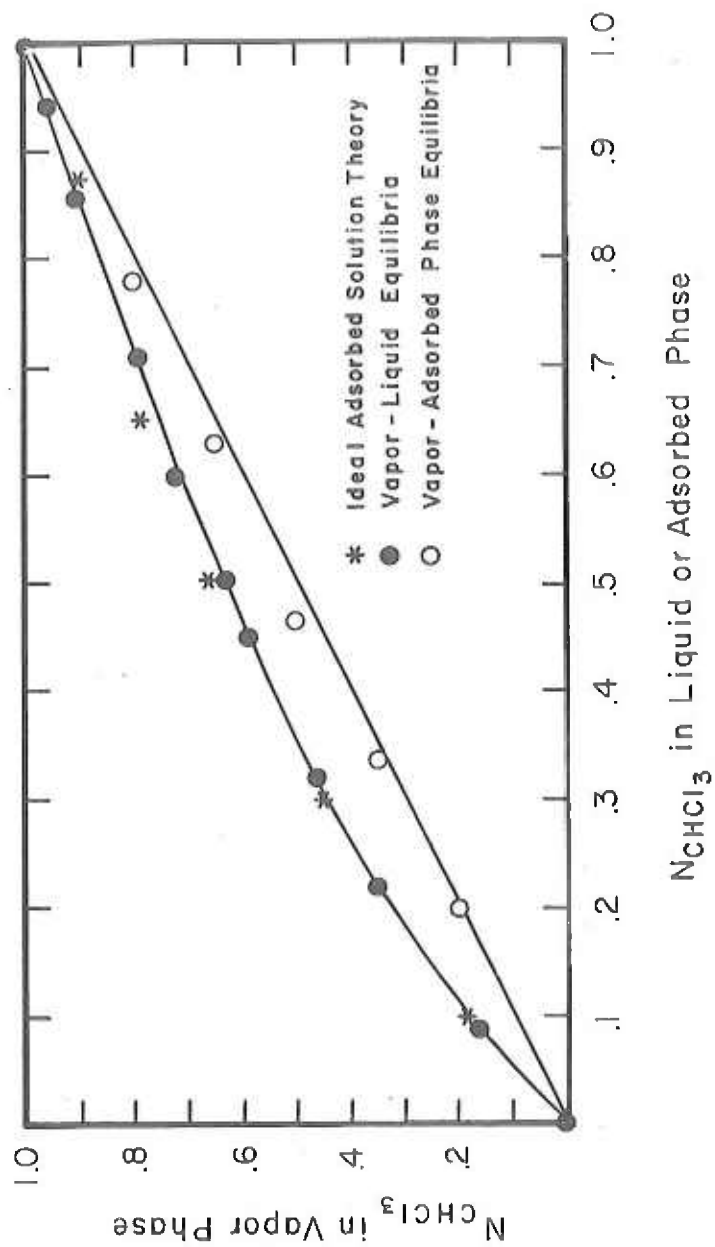


Figure 7. Vapor-Liquid and Vapor-Adsorbed Phase Equilibria for  $\text{CHCl}_3/\text{CCl}_4$  Binary Systems (BPL-Activated Carbon, 400  $\text{cm}^3/\text{min}$ , 25°C)

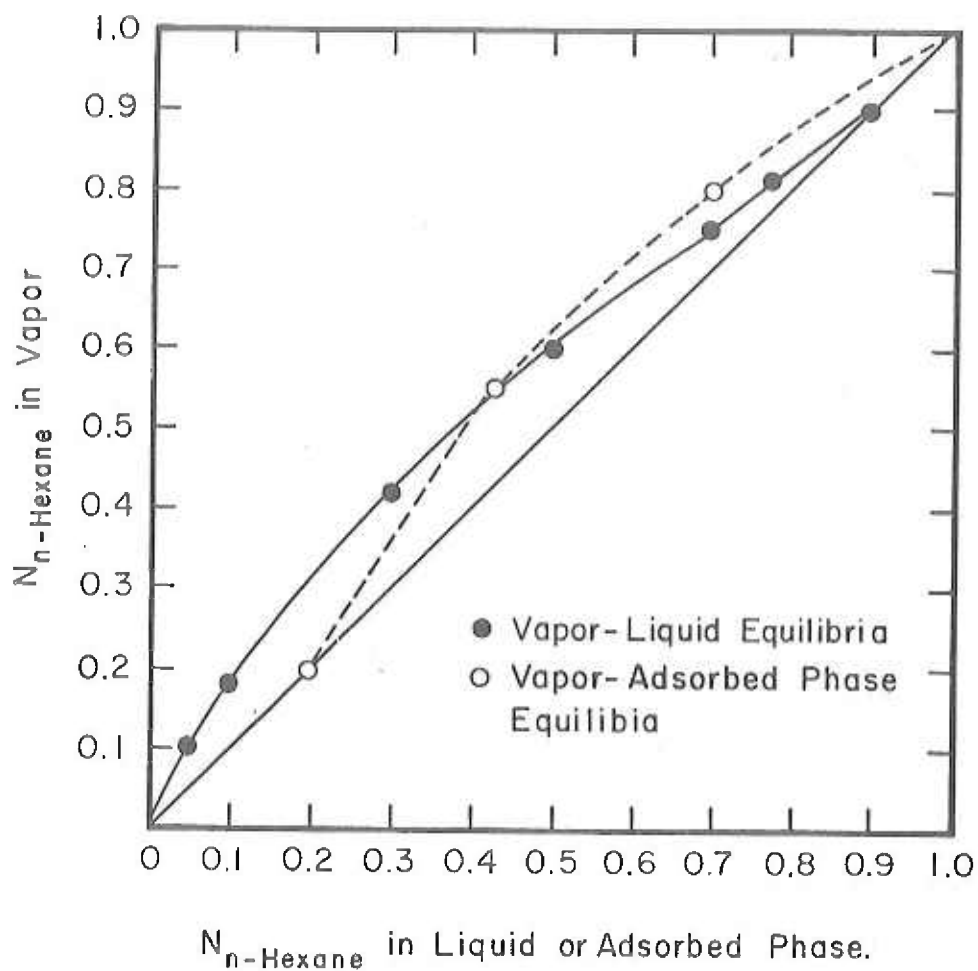


Figure 8. Vapor-Liquid and Vapor-Adsorbed Phase Equilibria for Benzene/  
n-Hexane Binary Systems (BPL-Activated Carbon, 400 cm<sup>3</sup>/min,  
25°C)

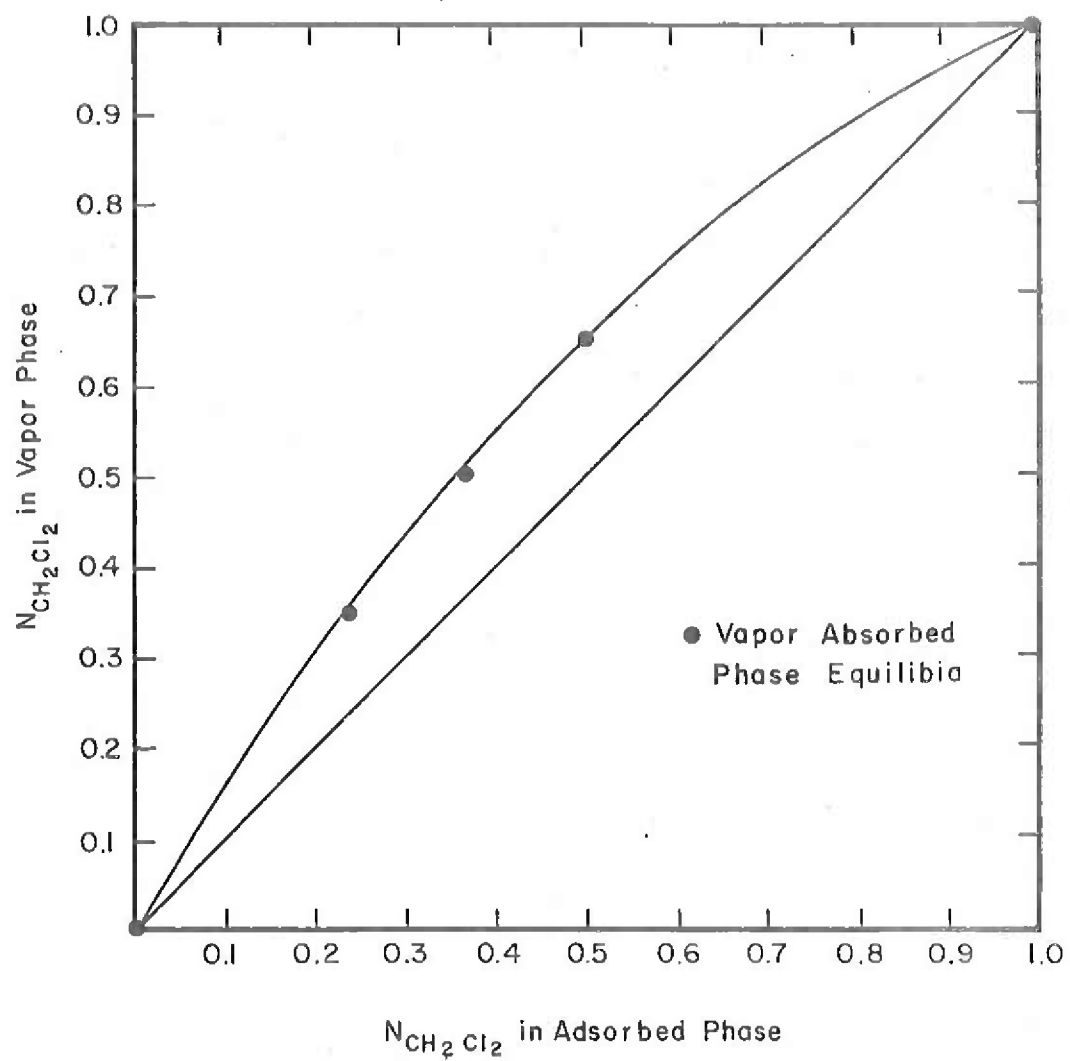


Figure 9. Vapor-Liquid and Vapor-Adsorbed Phase Equilibria for  $\text{CHCl}_2/\text{CHCl}_3$  Binary Systems (BPL-Activated Carbon,  $400 \text{ cm}^3/\text{min}$ ,  $25^\circ\text{C}$ )

this. Thus, the ideal adsorbed solution theory is not in good agreement with the experimental adsorption data in the  $\text{CHCl}_3/\text{CCl}_4$  system. However, if a liquid solution of  $\text{CHCl}_3/\text{CCl}_4$  is considered,<sup>20</sup> the relationship between the vapor composition and the liquid solution composition is the same as that predicted from ideal adsorbed solution theory. The discrepancy in the adsorption case may be due to the inability of the Wheeler equation to predict  $W_e$  values in the  $\text{CHCl}_3/\text{CCl}_4$  system. However, in the case of the n-hexane/benzene system, normal behavior is observed from 20 to 70 mole percent of n-hexane, i.e., the system behaves as a normal liquid-vapor equilibrium (see Figure 8). At lower than 20 mole percent n-hexane, the curve becomes very flat, indicating higher adsorption of n-hexane than expected from normal liquid-vapor equilibrium<sup>21</sup>. Figure 8 also shows that lower adsorption of n-hexane occurs at greater than 70 mole percent n-hexane.

In the case of the  $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$  system, the data covers a more limited concentration range and no conclusions can be drawn at the present time.

#### 5. RECOMMENDATIONS

Efforts within the last year have dealt with detailed studies of  $\text{CHCl}_3/\text{CCl}_4$  binary and single vapors with respect to equilibrium adsorption isotherms and the kinetics of adsorption on BPL-activated carbon. Additionally, preliminary results have been obtained in the cases of n-hexane/benzene and  $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$  binary and single vapors with respect to kinetics of adsorption.

For the next phase of the project several objectives have been formulated:

- a. Continuation of binary vapor adsorption studies on  $\text{CHCl}_3/\text{CCl}_4$ , n-hexane/benzene, and  $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$  vapor mixtures.



- b. Extension of the single vapor kinetic adsorption studies to several additional total pressures in order to obtain a complete isotherm.
- c. Further studies on  $\text{CHCl}_3$  single vapors and mixtures involving  $\text{CHCl}_3$ , in order to clarify the apparent inapplicability of the Wheeler equation to vapor systems which contain  $\text{CHCl}_3$  as a component.
- d. Application of the pore filling model, John's model, and the ideal adsorbed solution theory to the n-hexane/benzene and  $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$  binary systems.

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